

Characterization of the minimum energy paths and energetics for the reaction of vinylidene with acetylene

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The reaction of vinylidene (CH_2C) with acetylene may be an initiating reaction in soot formation. We report minimum energy paths and accurate energetics for a pathway leading to vinylacetylene and for a number of isomers of C_4H_4 . The calculations use complete active space self-consistent field (CASSCF) derivative methods to characterize the stationary points and internally contacted configuration interaction (ICCI) and/or coupled cluster singles and doubles with a perturbational estimate of triple excitations [CCSD(T)] to determine the energetics. We find an entrance channel barrier of about 5 kcal/mol for the addition of vinylidene to acetylene, but no barriers above reactants for the reaction pathway leading to vinylacetylene. © 1995 American Institute of Physics.

I. INTRODUCTION

The formation of the first aromatic ring is widely held to be the rate limiting step in the formation of soot in the combustion of aliphatic fuels. One mechanism for the formation of the first aromatic ring involves stepwise addition of acetylenes to give first C_4H_3 radical and then phenyl radical.¹ The interaction of two ground state acetylene molecules with each other is expected to be repulsive by either Woodward-Hoffman rules² or the orbital phase continuity principle,³ and in this work no low-energy pathway was found for the reaction of two ground state acetylenes. On the other hand, the reaction of vinylidene with acetylene is found to occur by a low-energy pathway as discussed here.

The vinylidene molecule has been studied extensively by both theory and experiment. The current state of knowledge has been summarized by Schaefer and co-workers.⁴ Vinylidene is found to be a shallow minimum on the C_2H_2 potential energy surface about 43 kcal/mol above acetylene and separated from acetylene by a barrier of about 3 kcal/mol (in addition to the exoergicity). The vinylidene molecule has been observed experimentally in the high resolution stimulated emission pumping spectrum of acetylene⁵ and in the ultraviolet photoelectron spectrum of CH_2C^- .^{6,7} The lifetime of vinylidene has been estimated to be 0.04–0.20 ps.

Vinylidene has also been proposed as an intermediate in the dimerization of acetylene. Kiefer *et al.*⁸ have proposed that the thermal decomposition of vinylacetylene involves an initial elimination of vinylidene followed by rapid rearrangement of the vinylidene to a second acetylene. The derived barrier for this process suggests that the reverse process of addition of vinylidene to acetylene has little or no barrier.

Many of the stationary point structures discussed here have also been considered by Melius *et al.*⁹ in their studies of the thermal decomposition of vinylacetylene and by Kollmar, Carrion, Dewar, and Bingham¹⁰ in their studies of the C_4H_4 potential energy surface. Recently the vinylvinylidene

species has been observed experimentally in the Lineberger group.¹¹

In Sec. II we discuss qualitative features of the reactions considered here. Section III discusses the technical details of the calculations, Sec. IV discusses the results, and Sec. V concludes the paper.

II. QUALITATIVE FEATURES

Figure 1 shows (in schematic form) the electronic structure of the stationary points along the minimum energy pathway from vinylidene plus acetylene to vinylacetylene, while Fig. 2 shows the geometries of each of the stationary points. Figure 1(a) shows the triple bond structure of acetylene, while Fig. 1(b) shows the electronic structure of vinylidene. In vinylidene one π bond is lost compared to acetylene, but there is a strong angular correlation effect of the carbene electron pair in the direction of the missing π bond. In the following it is useful to think of the electrons of the carbene electron pair as two sp^2 hybrid orbitals (referred to as lobes) which are singlet paired. Thus, the most important electron correlation effects for the vinylidene plus acetylene region of the potential energy surface are for the two π bonds in acetylene and the one π bond and the carbene pair in vinylidene (8 active electrons).

By analogy to the reaction of $\text{CH}({}^2\Pi) + \text{N}_2$,¹² the saddle point for the addition of vinylidene to acetylene involves a nearly parallel approach of the CH and acetylene as indicated in Fig. 1(c) (structure $sp1$). The electronic interaction involves the formation of a bond between one lobe of the carbene pair of vinylidene and one p orbital of the in plane π bond of acetylene. This arrangement allows a high overlap to also be maintained between the other lobe of the carbene pair and the other p orbital of the in plane π bond of acetylene. This leads to structure min1, the electronic structure of which is shown in Fig. 1(d). Figure 1(d) has two in plane singly occupied orbitals; these are singlet paired due to through bond coupling effects (i.e., the singlet is lower in energy than the triplet).

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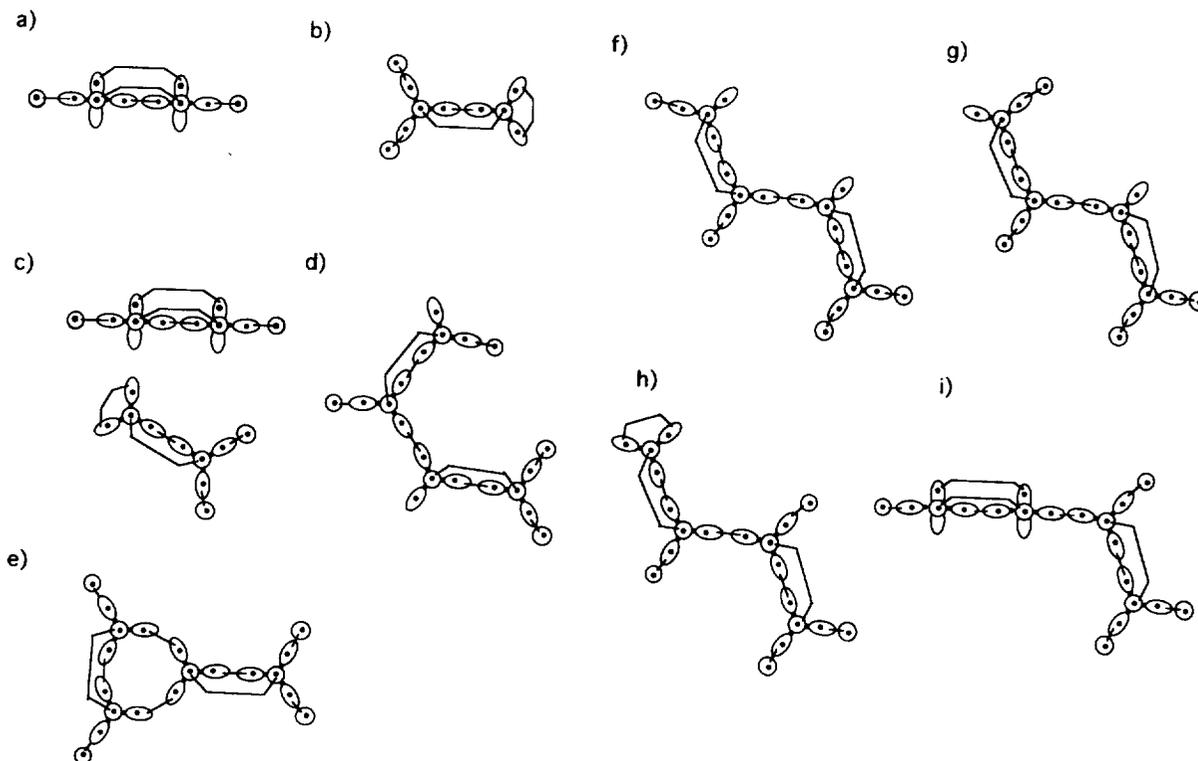


FIG. 1. The electronic structure of selected stationary points on the C_4H_4 potential energy surface.

The conversion from min1 to min2 (methylenecyclopropane) involves an inversion of the end CH group and a recoupling of the in-plane electrons, leading to the structure shown in Fig. 1(e). Min2 can open leading to min3, which is shown in Fig. 1(f). Min3 also has two in-plane singly occupied orbitals, which are singlet coupled. Inversion of the end CH group leads to min4, which is shown in Fig. 1(g). A 1,3-hydrogen shift converts min4 to min5 (vinylvinylidene), which is shown in Fig. 1(h). The end carbon of vinylvinylidene is carbene like and min5 can undergo a facile 1,2-hydrogen shift leading to vinylacetylene, which is shown in Fig. 1(i).

III. COMPUTATIONAL DETAILS

A number of different basis sets were used in these calculations. For the CASSCF derivative calculations, which were used to locate the stationary points, the valence double zeta set of Dunning and Hay¹³ was used. The basis set for C is the $(9s5p)/[3s2p]$ basis and the H basis is $(4s)/[2s]$, i.e., the polarization functions are omitted. The ICCI calculations used the Dunning correlation consistent polarized valence double zeta and triple zeta basis sets¹⁴ (cc-pVDZ and cc-pVTZ). The CASSCF is an 8 electron/8 orbital calculation with 4 a' and 4 a'' active orbitals. This calculation correlates the valence electrons which correspond to the four π electrons of acetylene and the two π and two carbene electrons of vinylidene for the acetylene plus vinylidene asymptote (see Sec. II). The subsequent ICCI calculations also were based on the 8/8 active space and included all reference configurations that can be constructed from this active space, with the constraint that no more than two electrons are allowed in the four weakly occupied orbitals. The CCSD(T) calculations were carried out with a [4321/321] ANO basis¹⁵ set (i.e., of pVTZ quality), using structures which were optimized at the SCF level using the 4-31G** basis set.

Calculations were also carried out for vinylidene, acetylene, and the saddle point connecting them. These calculations used the TZ+2P basis set CCSD geometries from Ref. 4. The calculations were based on a ten electron/ten orbital CASSCF calculation and subsequent ICCI calculation with the Dunning cc-pVTZ basis set.

The CASSCF gradient calculations used the SIRIUS/

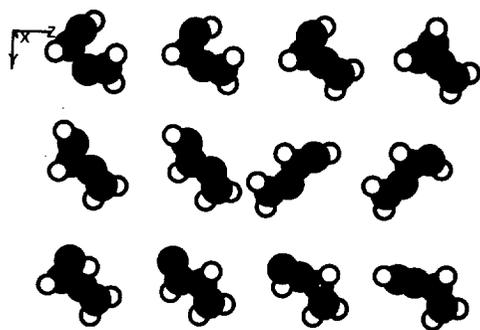


FIG. 2. Stationary point geometries for the minimum energy path leading from vinylidene plus acetylene to vinylacetylene.

Top row: $sp1$, min1, $sp2$, min2.
Middle row: $sp3$, min3, $sp6$, min4.
Bottom row: $sp5$, min5, $sp7$, min7.

TABLE I. Computed energetics for the vinylidene to acetylene rearrangement.

Geometry	ICCI(ICCI+Q+77)	ΔE^a	ZPE ^b	ΔE^a
<i>s.p.</i>	-77.101 46(-0.113 01)	3.1	0.021 02	1.3
vinylidene	-77.106 19(-0.117 99)	0.0	0.023 91	0.0
acetylene	-77.177 77(-0.187 87)	-43.9		

^aEnergy difference in kcal/mol including zero-point energy.

^bZero-point energy in E_h .

ABACUS system of programs,¹⁶ while the ICCI calculations were carried out with MOLPRO.^{17,18} The active spaces for these calculations are as discussed above. The CCSD calculations were carried out with TITAN.¹⁹ All electrons were correlated except for the C 1s like electrons. A multireference analog of the Davidson's correction²⁰ was added to the ICCI energies and is denoted by +Q.

The saddle points were located using an image surface method.²¹ The image surface minimization method uses a topological transformation of the original surface so that a saddle-point search becomes a minimization on the image surface. The image surface approach used here employs a quadratic approximation to the original surface and a trust-region-based optimization. In practice it is found that this method works well provided the starting geometry is within the region of the surface with the correct eigenvalue structure (one negative eigenvalue). Once the saddle points are located the minima which are connected by each saddle point are determined by following the gradient in both directions away from the saddle point. These walks are started by displacing the system slightly in the direction of the negative eigenvalue of the Hessian matrix.

IV. DISCUSSION

Table I shows computed energetics for vinylidene, acetylene, and the saddle point connecting them. As discussed in Sec. III, the geometries and harmonic frequencies are taken from the CCSD calculations with a TZ+2P basis set of Ref. 4. The zero-point effects were estimated as 1/2 the sum of

TABLE II. Energies for stationary points on the C_4H_4 surface.

Geometry	ICCI(ICCI+Q+154)	ZPE ^b	ΔE (kcal/mol) ^a
Reactants	-154.094 91(-0.149 60)	0.052 76	0.0
<i>sp1</i>	-154.085 54(-0.143 84)	0.055 65	5.4
min1	-154.120 12(-0.181 96)	0.060 29	-15.6
<i>sp2</i>	-154.124 58(-0.185 35)	0.058 36	-18.9
min2	-154.187 02(-0.244 77)	0.062 45	-53.6
<i>sp3</i>	-154.098 39(-0.161 28)	0.059 47	-3.1
min3	-154.099 48(-0.165 10)	0.060 20	-5.1
<i>sp6</i>	-154.086 35(-0.152 58)	0.056 95	0.8
min4	-154.098 46(-0.163 14)	0.059 99	-4.0
<i>sp8</i>	-154.074 07(-0.136 55)	0.054 01	9.0
<i>sp5</i>	-154.112 70(-0.174 64)	0.057 70	-12.6
min5	-154.158 02(-0.214 38)	0.061 07	-35.4
<i>sp7</i>	-154.155 51(-0.212 87)	0.057 30	-36.9
min7	-154.230 50(-0.285 86)	0.063 28	-78.9

^aEnergy difference in kcal/mol including zero-point energy.

^bZero-point energy in E_h .

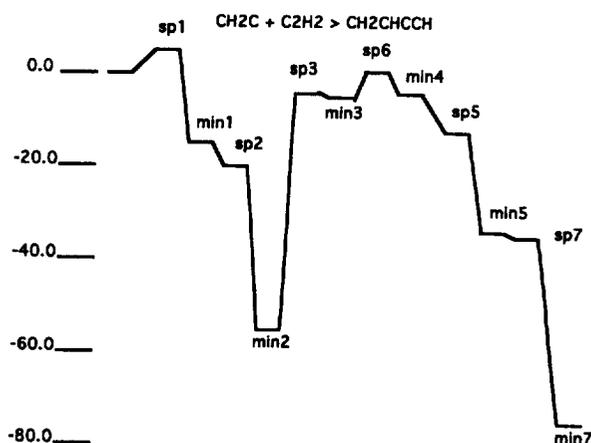


FIG. 3. Computed energetics for the minimum energy path leading from vinylidene plus acetylene to vinylacetylene. The energetics are from ICCI calculations, using the Dunning cc-pVDZ basis set and include a correction for zero-point effects based on harmonic frequencies derived from an (8/8) CASSCF calculation (see the text).

the harmonic frequencies and these are included in the relative energies which are given in the last column of Table I. Thus, the relative energies are appropriate for comparison to experimental results corrected to 0 K. These results show a barrier height of 3.1 kcal/mol, which is reduced to 1.3 kcal/mol when zero-point effects are included. This is in agreement with the best estimate of 3 kcal/mol for the classical barrier height made in Ref. 4.

Table II shows the computed ICCI energies obtained at the optimized CASSCF geometries. The energetics for the pathway leading from vinylidene plus acetylene to vinylacetylene are also shown in Fig. 3. Tables AI and AII in the PAPS material²² give the harmonic frequencies and the Cartesian coordinates for the CASSCF optimized structures, respectively.

From Table II it is seen that the barrier for addition of vinylidene to acetylene is 5.4 kcal/mol. Since the addition of CH to acetylene involves no barrier,²³ it is probable that the barrier in vinylidene plus acetylene arises from nonbonded repulsions with the CH bonds of the CH_2 group. This is evident in the saddle point geometry, shown in Fig. 2, which has the CC bond of vinylidene tipped away from the approximately parallel orientation with the CC bond in acetylene that was seen in the case of CH addition. This saddle point was obtained in C_s symmetry. From Table AI it is seen

TABLE III. ICCI energies at selected steps along the minimum energy pathway from min5 to min7 via *sp7*.

Geometry ^a	ICCI(ICCI+Q+154)
min5	-154.158 02(-0.214 38)
step8	-154.157 37(-0.214 07)
step5	-154.155 94(-0.213 56)
step2	-154.155 27(-0.213 04)
<i>sp7</i>	-154.155 51(-0.212 87)
step02	-154.157 47(-0.214 23)
step04	-154.164 15(-0.220 23)

^aCartesian coordinates for the geometries are given in the PAPS.

TABLE IV. CCSD(T) energies for some C₄H₄ isomers.

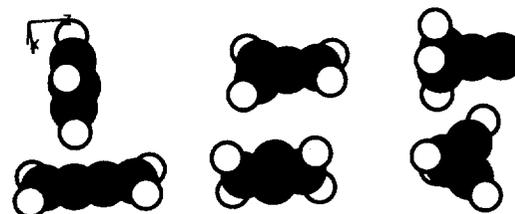
Structure	CCSDT(T)	ZPE ^a	ΔE	$\Delta H_f, 0\text{ K}$
acetylene + acetylene	-154.390 854	0.052 840	-42.1	108.7 ^b
acetylene + vinylidene	-154.320 570	0.049 690	0.00	150.8
vinylacetylene	-154.459 403	(0.059 60)	-80.9	72.2
cyclobutadiene (min8)	-154.404 368	0.059 543	-46.4	104.4
methylenecyclopropene (min2)	-154.420 193	0.058 786	-56.8	94.0
carbenecyclopropane (min9)	-154.369 844	0.058 752	-25.2	125.6
butatriene (min 10)	-154.446 762	0.058 073	-73.9	76.9
bicyclobutene (min11)	-154.351 545	0.059 298	-13.4	137.4
tetrahydrane (min12)	-154.359 985	0.058 281	-19.3	131.5

^aZero-point energy obtained as 1/2 the sum of the SCF frequencies $\times 0.9$. The vinylacetylene zero-point energy is from the CASSCF frequencies without scaling.

^bAcetylene heat of formation is from Ref. 24.

that there is a small imaginary frequency corresponding to symmetry breaking. Thus, the true saddle point may be non-planar. This effect, which was not investigated further, could lower the barrier for addition slightly. The remaining saddle points are true saddle points i.e., they have only one imaginary frequency.

From Fig. 3 it is seen that *sp2* is below min1 at the ICCI+*Q* level of theory. This suggests that on the ICCI surface the energy decreases monotonically from *sp1* to min2. Min2 (methylenecyclopropene) is a deep minimum on the surface. Min3 appears to be a shallow minimum with saddle points *sp3* and *sp6* on either side of it. However, it is monotonically down hill from *sp6* to min5 (vinylvinylidene). *sp7* is 0.9 kcal/mol above vinylvinylidene, but with inclusion of zero-point effects *sp7* is 1.5 kcal/mol below vinylvinylidene. Negative ion photodetachment experiments indicate that vinylvinylidene has a short lifetime with respect to the 1,2-hydrogen shift leading to vinylacetylene. This would seem to imply at least a small barrier for conversion of vinylvinylidene to vinylacetylene. In order to provide more infor-

FIG. 4. Stationary point structures for some C₄H₄ isomers.

Top row: min8 (cyclobutadiene), min2 (methylenecyclopropene), min9 (carbenecyclopropane).

Bottom row: min10 (butatriene), min11 (bicyclobutene), min12 (tetrahydrane).

mation on this point, calculations were carried out to characterize the minimum energy path connecting vinylvinylidene to vinylacetylene. The reaction pathway was obtained by following the gradient in both directions away from *sp7*. The Cartesian coordinates at the steps on the pathway are given in the PAPS,²² while the ICCI energies at selected points along the pathway are given in Table III. From Table III it is seen that the maximum in the energy along the path occurs very near *sp7*. Thus, the best estimate of the non-zero-point corrected barrier height is 0.9 kcal/mol. This is significantly smaller than the barrier height of 3.1 kcal/mol obtained for the 1,2 hydrogen shift in vinylidene.

From Table II the barrier for the conversion of vinylacetylene to vinylidene plus acetylene is 84.3 kcal/mol. This is in reasonable agreement with the estimated activation energy of 79.5 kcal/mol for the dissociation of vinylacetylene to two acetylenes by Kiefer *et al.*⁸

Table IV shows relative energies for a number of isomers of C₄H₄ obtained by the CCSD(T) method and Table V shows energies for calculations on the same structures using the ICCI method. Tables AIII and AIV of the PAPS²² give the Cartesian coordinates and harmonic frequencies for these stationary points. Figure 4 shows the geometries of these isomers. The CCSD(T) calculations were carried out with

TABLE V. ICCI energies for some C₄H₄ isomers.

Structure	pVDZ	ΔE	pVTZ	ΔE
	ICCI(ICCI+ <i>Q</i>)		ICCI(ICCI+ <i>Q</i>)	
acetylene + vinylidene	-154.089 73(-0.141 83)	0.0	-154.221 95(-0.289 20)	0.0
cyclobutadiene (min8)	-154.171 69(-0.228 17)	-47.2	-154.300 38(-0.371 59)	-45.5
methylenecyclopropene (min2)	-154.184 14(-0.240 27)	-55.3	-154.316 50(-0.387 56)	-56.0
carbenecyclopropane (min9)	-154.138 66(-0.194 83)	-26.8	-154.262 86(-0.335 73)	-23.5
butatriene (min10)	-154.212 89(-0.267 60)	-72.9	-154.344 71(-0.414 36)	-73.3
bicyclobutene (min11)	-154.114 26(-0.174 37)	-13.6	-154.242 77(-0.317 68)	-11.8
tetrahydrane (min12)	-154.115 91(-0.175 40)	-14.9	-154.249 37(-0.324 32)	-16.6
vinylvinylidene	-154.158 02(-0.214 38)	-39.8	-154.279 12(-0.350 94)	-33.8
vinylacetylene	-154.230 50(-0.285 86)	-83.4	-154.360 08(-0.427 62)	-80.6

ANO basis sets of polarized triple zeta quality while the ICCI calculations made use of the cc-pVDZ and cc-pVTZ basis sets. The zero-point energies were obtained from the SCF harmonic frequencies scaled by 0.9. In the case of vinylvinylidene and vinylacetylene the SCF zero-point correction was estimated from the CASSCF harmonic frequencies scaled by 0.942. This value is the scale factor needed to give the same zero point energy for the vinylidene plus acetylene asymptote as that given from the scaled SCF frequencies.

A number of interesting structures are shown in Tables IV and V and Fig. 4. Those with energy below two acetylenes (energy relative to vinylidene+acetylene in parentheses) are vinylacetylene (-80.9), butatriene (-73.9), methylenecyclopropene (-56.8), and cyclobutadiene (-46.4). From the comparison of Tables IV and V it is seen that there is good agreement between the ICCI and CCSD(T) results. The ordering of these structures is in at least qualitative accord with the results of Ref. 10. A saddle point (*sp8*) was found connecting min4 to butatriene; however, the barrier height of 9.0 kcal/mol, with respect to reactants, suggests that this would be a minor pathway.

Melius *et al.*⁹ reported computed reaction pathways for the thermal decomposition of vinylacetylene. These authors discussed a carbene mechanism involving vinylidene but do not show the vinylidene plus acetylene asymptote in Fig. 2 of their paper. (Presumably because the vinylidene would rapidly convert to acetylene in the thermal decomposition process.) In Fig. 2 of Ref. 9 they show a barrier leading from methylenecyclopropene to two acetylenes. However, it is likely that this process proceeds through vinylidene plus acetylene. Positioning the vinylidene plus acetylene asymptote 43 kcal/mol above the asymptote for two acetylenes, this figure is consistent with a small barrier separating methylenecyclopropene from vinylidene plus acetylene. These authors also show a barrier between methylenecyclopropene and vinylacetylene as well as a shoulder on the curve. It is tempting to speculate that the shoulder corresponds to vinylvinylidene. However, this is not discussed in their paper.

V. CONCLUSIONS

We report reaction pathways and accurate energetics (from CASSCF/gradient plus ICCI calculations with a cc-pVDZ basis set) for the reaction pathway connecting vinylidene plus acetylene to vinyl acetylene. There is a barrier of about 5 kcal/mol for the addition of vinylidene to acetylene but the remaining barriers are all lower than this. The calculations suggest that vinylvinylidene represents at most a shallow minimum on the potential energy surface, which can undergo a facile 1,2-hydrogen shift leading to vinylacetylene. These potential surface features are at least in semi-quantitative agreement with the BAC/MP-4 calculations of Melius *et al.* for the thermal decomposition of vinylacetylene.

We also report CCSD(T) calculations with an ANO basis set of pVTZ quality for a number of minima on the C₄H₄

PES. Those with energy below two acetylenes (energy relative to vinylidene+acetylene in parentheses) are vinylacetylene (-80.9), butatriene (-73.9), methylenecyclopropene (-56.8), and cyclobutadiene (-46.4).

The calculations predict a separation between acetylene and vinylidene of 43.9 kcal/mol and a barrier to isomerization of vinylidene to acetylene of 1.3 kcal/mol (including zero-point effects) in good agreement with the published results of Ref. 4.

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